

**Q. 2.8** A monochromatic beam of X-rays of wavelength  $1.24 \text{ \AA}$  is reflected by cubic crystal of KCl. Determine the inter planar distances for (100), (110) and (111) planes. Given density of KCl =  $1980 \text{ kg/m}^3$  and molecular weight  $M = 74.5 \text{ kg}$ . Avogadro's number  $N = 6.02 \times 10^{26} \text{ kg mole}^{-1}$ . (Bang. U. 1994)

**Ans.** For a cubic crystal, we have

$$a^3 = \frac{nM}{N\rho}$$

where  $a$  is the lattice constant,  $n$  the number of molecule in a unit cell,  $M$  the molecular weight,  $N$  Avogadro's number and  $\rho$  the density.

For KCl cubic crystal  $n = 4$

$$a^3 = \frac{4 \times 74.5}{6.023 \times 10^{26} \times 1.98 \times 10^3} = 25 \times 10^{-30}$$

or

$$a = [250 \times 10^{-30}]^{1/3} = 6.3 \times 10^{-10} \text{ m}$$

Now

$$d_{100} = \frac{a}{\sqrt{1^2 + 0^2 + 0^2}} = a = 6.3 \times 10^{-10} \text{ m}$$

$$d_{110} = \frac{a}{\sqrt{1^2 + 1^2 + 0^2}} = \frac{a}{\sqrt{2}} = \frac{6.3}{\sqrt{2}} \times 10^{-10} = 4.45 \times 10^{-10} \text{ m}$$

$$d_{111} = \frac{a}{\sqrt{1^2 + 1^2 + 1^2}} = \frac{a}{\sqrt{3}} = \frac{6.3}{\sqrt{3}} \times 10^{-10} = 3.63 \times 10^{-10} \text{ m}$$

**Q. 2.9** From the following data calculate the wavelength of neutron beam and its speed. Spacing between successive (100) planes =  $3.84 \text{ \AA}$ ; grazing angle  $30^\circ$ ; order of Bragg reflection = 1.

(H.P.U. 1999, 1995, 1994)

**Ans.** According to Bragg's relation

$$2d \sin \theta = n\lambda$$

Here

$$d = 3.84 \text{ \AA} = 3.84 \times 10^{-10} \text{ m}, \theta = 30^\circ; \sin 30^\circ = \frac{1}{2}; n = 1$$

$$\therefore 2 \times 3.84 \times 10^{-10} \times \frac{1}{2} = 1 \times \lambda$$

or

$$\lambda = 3.84 \times 10^{-10} \text{ m} = 3.84 \text{ \AA}$$

According to de-Broglie relation

$$\lambda = \frac{h}{p} = \frac{h}{mv} \text{ where } h \text{ is Planck's constant having a value } 6.62 \times 10^{-34} \text{ Js and neutron mass } m = 1.67 \times 10^{-27} \text{ kg}$$

$$\therefore v = \frac{h}{m\lambda} = \frac{6.62 \times 10^{-34}}{1.67 \times 10^{-27} \times 3.84 \times 10^{-10}} = 1.03 \times 10^3 \text{ ms}^{-1}$$

**Q. 2.10** Derive Laue's equations of diffraction of X-rays and obtain Bragg's diffraction condition from them.

(G.N.D.U. 2004, 2003, 2002, 2001, 1999, 1996; H.P.U. 2003, 2001, 1996; P.U. 2001, 1995; Pbi. U. 2002; Meerut U. 2001; Cal. U. 2001; M.D.U. 1999; Luck. U. 199)

**Ans. Laue's equations.** Laue's diffraction equations give the conditions under which X-rays scattered from different atoms of a crystal combine to form a diffracted beam. For this purpose  $v$

study the X-ray diffraction pattern produced by identical scattering centres located at the *lattice points* of a three dimensional crystal lattice. Let  $P_1$  and  $P_2$  be two such lattice points separated by a vector  $\vec{r}$ . Suppose a parallel beam of X-rays is incident on  $P_1P_2$  along the direction of unit vector  $\hat{i}$ . The scattered beam is also parallel and let it be in any arbitrary direction given by unit vector  $\hat{s}$ . Draw  $P_1A$  perpendicular to the incident wave direction and  $P_2B$  perpendicular to the scattered wave direction, then  $P_1A$  is incident and  $P_2B$  the scattered wave front. The path difference between the two scattered waves – one scattered from  $P_2$ , and the other scattered from  $P_1$  is given by

$$P_2A - P_1B = \vec{r} \cdot \hat{i} - \vec{r} \cdot \hat{s} = \vec{r} \cdot (\hat{i} - \hat{s}) = \vec{r} \cdot \vec{S}$$

where  $\vec{S} = (\hat{i} - \hat{s})$  is a vector in the direction of the normal to the reflecting plane.

If  $\theta$  is the angle that the incident beam makes with the reflecting plane, then the angle that the scattered (reflected) beam makes with the reflecting plane is also equal to  $\theta$  and the angle between the unit vectors  $\hat{i}$  and  $\hat{s} = 2\theta$  as shown in Fig. 2.4.

$$\therefore |\vec{S}| = 2 \sin \theta \quad [\because \hat{i} \text{ and } \hat{s} \text{ are unit vectors}]$$

The phase difference between the waves scattered at the lattice points  $P_1$  and  $P_2$  is given by

$$\phi = \frac{2\pi}{\lambda} (\vec{r} \cdot \vec{S})$$

The intensity of the diffracted beam is a *maximum* in the direction in which  $\phi$  is an integral multiple of  $2\pi$ .

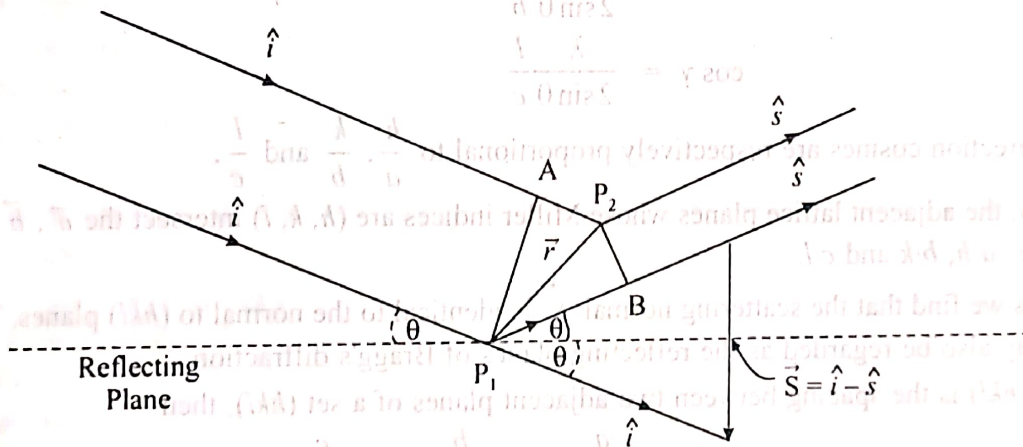


Fig. 2.4

If  $\vec{a}$ ,  $\vec{b}$  and  $\vec{c}$  are the primitive lattice vectors of the point  $P_2$  with respect to the point  $P_1$ , then

$$\vec{r} = \vec{a} + \vec{b} + \vec{c}$$

and the above condition can be put in the form of three separate conditions i.e.,

$$\phi_a = \frac{2\pi}{\lambda} (\vec{a} \cdot \vec{S}) = 2\pi h \quad \dots(i)$$

$$\phi_b = \frac{2\pi}{\lambda} (\vec{b} \cdot \vec{S}) = 2\pi k \quad \dots(ii)$$

$$\phi_c = \frac{2\pi}{\lambda} (\vec{c} \cdot \vec{S}) = 2\pi l \quad \dots(iii)$$

and where  $h, k, l$  are integers and  $\phi_a, \phi_b$  and  $\phi_c$  are phase differences between the waves scattered from the two ends of the primitive lattice vectors  $\vec{a}$ ,  $\vec{b}$  and  $\vec{c}$  respectively.



If  $\alpha, \beta, \gamma$  are the angles between the normal to the reflecting plane and  $\vec{a}, \vec{b}$  and  $\vec{c}$  axes respectively, then

$$\vec{a} \cdot \vec{S} = |\vec{a}| |\vec{S}| \cos \alpha = 2a \sin \theta \cos \alpha$$

$$\vec{b} \cdot \vec{S} = |\vec{b}| |\vec{S}| \cos \beta = 2b \sin \theta \cos \beta$$

$$\vec{c} \cdot \vec{S} = |\vec{c}| |\vec{S}| \cos \gamma = 2c \sin \theta \cos \gamma$$

From (i), (ii) and (iii), we have

$$\vec{a} \cdot \vec{S} = h\lambda, \quad \vec{b} \cdot \vec{S} = k\lambda \quad \text{and} \quad \vec{c} \cdot \vec{S} = l\lambda$$

$$2a \sin \theta \cos \alpha = h\lambda \quad \dots (iv)$$

$$2b \sin \theta \cos \beta = k\lambda \quad \dots (v)$$

$$2c \sin \theta \cos \gamma = l\lambda \quad \dots (vi)$$

These are the Laue's equations for X-ray diffraction.

**Derivation of Bragg's relation from Laue's equations.** If  $\theta$  gives the direction of Bragg diffraction for a wavelength  $\lambda$ , then direction cosines of  $\vec{S}$  the scattering normal from equations (iv), (v) and (vi) are given by

$$\cos \alpha = \frac{\lambda}{2a \sin \theta} \frac{h}{\lambda}$$

$$\cos \beta = \frac{\lambda}{2b \sin \theta} \frac{k}{\lambda}$$

$$\cos \gamma = \frac{\lambda}{2c \sin \theta} \frac{l}{\lambda}$$

i.e., the direction cosines are respectively proportional to  $\frac{h}{a}, \frac{k}{b}$  and  $\frac{l}{c}$ .

Now, the adjacent lattice planes whose Miller indices are  $(h, k, l)$  intersect the  $\vec{a}, \vec{b}, \vec{c}$  axes at intervals  $a/h, b/k$  and  $c/l$ .

Thus we find that the scattering normal  $\vec{S}$  is identical to the normal to  $(hkl)$  planes. The  $(hkl)$  planes may also be regarded as the reflecting planes of Bragg's diffraction.

If  $d(hkl)$  is the spacing between two adjacent planes of a set  $(hkl)$ , then

$$d(hkl) = \frac{a}{h} \cos \alpha = \frac{b}{k} \cos \beta = \frac{c}{l} \cos \gamma$$

According to Laue's equations

$$\frac{a}{h} \cos \alpha = \frac{b}{k} \cos \beta = \frac{c}{l} \cos \gamma = \frac{\lambda}{2 \sin \theta}$$

$\therefore$  Laue's equations can be put in the form

$$d(hkl) = \frac{\lambda}{2 \sin \theta}$$

or

$$2d(hkl) \sin \theta = \lambda$$

The integers  $h, k, l$  of Laue's equation are not necessarily identical with Miller indices of an actual crystal plane but these integers may contain a common factor say  $n$ , while in the indices the common factor has been eliminated.

Introducing the common factor  $n$ , we have

$$2d \sin \theta = n\lambda$$

where  $d$  is the spacing between adjacent planes with Miller indices  $\frac{h}{n}, \frac{k}{n}$  and  $\frac{l}{n}$ . The equation  $2d \sin \theta = n\lambda$  is Bragg's relation for an angle  $\theta$  between the incident beam and the reflecting plane.

Q. 2.11 (a) Name the standard experimental methods of X-ray diffraction.

(M.D.U. 2000; Pbi. U. 2000; G.N.D.U. 2000, 1995; H.P.U. 1997, 1993; P.U. 2000, 1995)

(b) Describe the various experimental X-ray diffraction methods for study of crystal structure. (H.P.U. 2002; G.N.D.U. 2001)

OR

Describe in detail (i) Laue's method.

(P.U. 2002, H.P.U. 1996)

(ii) Rotating crystal method. How do layer lines form?

(Pbi. U. 2004, 2003, 2002, 2000; G.N.D.U. 1995; P.U. 1991; Meerut U. 2002)

(iii) Powder method. The diameter of a powder camera is 57.3 mm or a multiple of that.

Explain. (Cal. U. 2002; Bang. U. 2001, 1994, 1992; G.N.D.U. 1996; Meerut U. 2002)

(c) Describe the usefulness of Laue's, powder and rotating crystal methods in the study of crystal structure. (P.U. 2000; G.N.D.U. 2000; H.P.U. 2000, 1996; Luck.U. 1996, 1994)

Ans. (a) Experimental X-ray diffraction methods. Diffraction of X-rays by the periodic lattice of a crystal provides a method of studying the crystal structure. Bragg's formula gives a simple relation between wavelength of X-rays  $\lambda$ , and angle of diffraction  $\theta$ . It states

$$2d \sin \theta = n\lambda$$

where  $d$  is the spacing between parallel atomic planes and  $n$  the order of diffraction maxima. For an experimental study the values of  $\lambda$  and  $\theta$  must be matched in accordance with this relation either by varying  $\lambda$  or  $\theta$ .

The standard experimental methods are:

✓(i) *Laue's method*. In this method a *single* crystal is held stationary in a beam of X-rays having continuous wavelength. The crystal selects and produces diffraction corresponding to discrete values of  $\lambda$  for which planes of spacing  $d$  exist and angle of incidence  $\theta$  satisfies Bragg's relation.

✓(ii) *Rotating crystal method*. In this method a *single* crystal is rotated about a fixed axis in a beam of monochromatic X-rays. The variation of  $\theta$  brings different atomic planes into position for Bragg reflection.

✓(iii) *Powder method*. In this method a *powdered* sample of crystalline material is placed in a fixed position in a monochromatic beam. Among the distribution of various crystalline orientations there will be some for which the angle of incidence satisfies Bragg's law. We shall describe these method in detail.

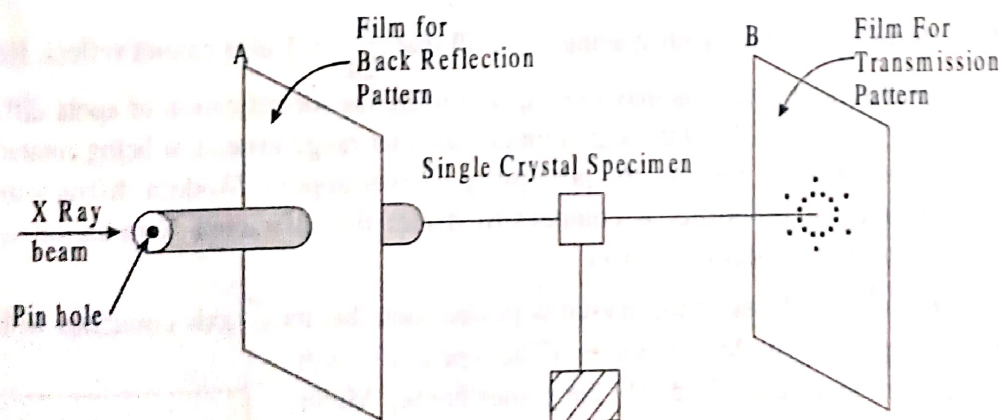


Fig. 2.5

(b) (i) **Laue's method**. Laue's X-ray camera consists of a source producing X-rays of continuous wavelength over a wide range (perhaps from  $0.2\text{\AA}$  to  $2\text{\AA}$ ), a pin hole collimator which produces a very fine narrow beam, a single crystal specimen not more than one mm in size held



stationary in a stand and two flat films on which the diffraction patterns are recorded as shown in Fig. 2.5. The film A records the back reflection pattern and the film B records the transmission pattern.

The crystal selects and diffracts the discrete values of  $\lambda$  for which planes exist of spacing  $d$  and of incidence angle  $\theta$  satisfying Bragg's relation. The diffraction pattern consists of a series of spots known as *Laue spots* showing the symmetry of the crystal. If a crystal with four-fold axis of symmetry is oriented with the axis parallel to the beam, the Laue pattern will show four-fold symmetry. This feature makes the Laue method specially useful for checking the orientation of crystals in solid state experiments.

(ii) **Rotating crystal method.** In the rotating crystal method, a single crystal (the dimensions of which are generally not greater than 1 mm) is rotated about a fixed axis in a beam of monochromatic X-rays. (The incident beam is made monochromatic by using a monochromatic filter or by reflection from an earlier crystal). The variation in the angle brings different atomic planes into position for reflection. The film is mounted in a cylindrical holder concentric with a rotating spindle on which the single crystal specimen is mounted.

As the crystal is rotated, the X-ray beam undergoes diffraction from a given crystal plane when the value of  $\theta$  satisfies Bragg's relation for the wavelength of X-rays used. Beams from all planes parallel to the vertical rotation axis will lie in the horizontal plane. Planes with other orientations will reflect in layers above and below the horizontal plane. The reflected spots form parallel lines called '*layer lines*'. As the wavelength is known the spacing  $d$  can be calculated using Bragg's relation  $2d \sin \theta = n\lambda$ .

Fig. 2.6

It may be noted that plane which always contains the incident beam during the whole rotation cannot reflect. Similarly a plane with spacing so small that  $\frac{\lambda}{2d} > 1$  also cannot reflect. Reflections from planes in different orientations may overlap and make the identification of spots difficult. For this purpose the crystal is oscillated through a limited angular range instead of being rotated through full  $360^\circ$ . The limited range reduces the possibility of overlapping. Modern diffractometers use scintillation counters or proportional counters to detect the diffracted X-radiation and allow automatic recording and collection of data.

**Formation of layer lines.** If the crystal is placed such that its  $\vec{c}$  axis coincides with the axis of rotation, all the planes with Miller indices of the type  $(h k 0)$  will produce the *central layer line*. Similarly the planes having Miller indices of the type  $(h k 1)$  and  $(h k \bar{1})$  will produce the layer lines above and below the central line as shown in Fig. 2.6 (a). The vertical spacing between the layer lines depends upon the distance between the lattice points along the  $\vec{c}$  axis. Thus the distance  $\vec{c}$  or translation vector  $\vec{c}$  can be measured from the photographic film. Similarly, by mounting the

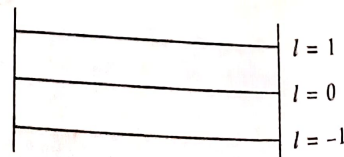


Fig 2.6(a)

Crystal Diffraction and Recip

crystal along  $\vec{a}$  and  $\vec{b}$  axes the dimensions of the unit c

(iii) **Powder method.**

of the crystal structure of s specimen is contained in a cylindrical type camera fitt

The distribution of chromatic X-radiation is from such individual mi which happen to be or planes making an angle beam satisfying Bragg's the wavelength  $\lambda$  of the The diffracted rays specimen along direc generate a number concentric with the dire original beam and make with it, where  $\theta$  is Bray cones intercept the film concentric rings. The rotated slowly during ensure that all sets of p

**Diameter of the pattern,** let  $R$  be the ra arcs corresponding to shown in Fig. 2.7(a) i

From the fig



crystal along  $\vec{a}$  and  $\vec{b}$  axes respectively the translation vectors  $\vec{a}$  and  $\vec{b}$  can be measured and thus the dimensions of the unit cell can be determined.

(iii) **Powder method.** This method was devised by Debye and Scherrer for the determination of the crystal structure of small grained crystallites or finely powdered poly-crystalline solids. The specimen is contained in a thin walled capillary tube held in a movable mount at the centre of a cylindrical type camera fitted with a photographic film inside as shown.

The distribution of crystallite orientations being nearly continuous the incident monochromatic X-radiation is diffracted from such individual micro-crystals which happen to be oriented with planes making an angle  $\theta$  with the beam satisfying Bragg's relation for the wavelength  $\lambda$  of the X-radiation. The diffracted rays leave the specimen along directions which generate a number of cones concentric with the directions of the original beam and make an angle  $2\theta$  with it, where  $\theta$  is Bragg angle. The cones intercept the film in a series of concentric rings. The specimen is rotated slowly during exposure to ensure that all sets of possible planes face the incident X-ray beam.

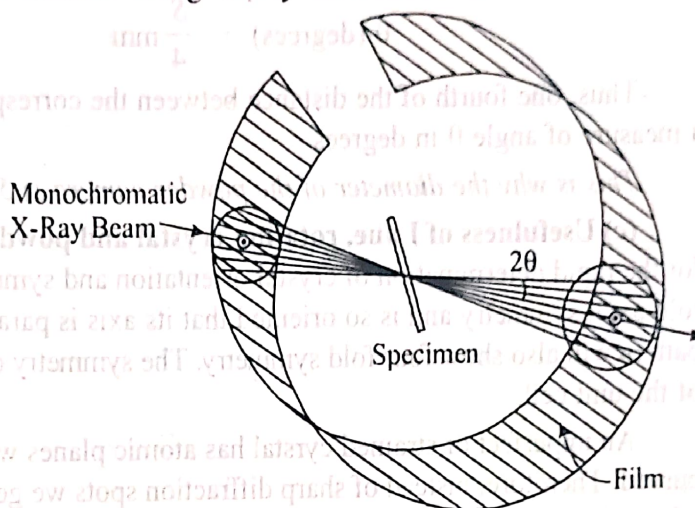


Fig. 2.7

**Diameter of the powder camera.** To determine the crystal structure from the diffraction pattern, let  $R$  be the radius of the camera and  $S$  be the distance on the film between the diffraction arcs corresponding to a particular plane, then the full opening angle of the corresponding cone as shown in Fig. 2.7(a) is  $4\theta$ .

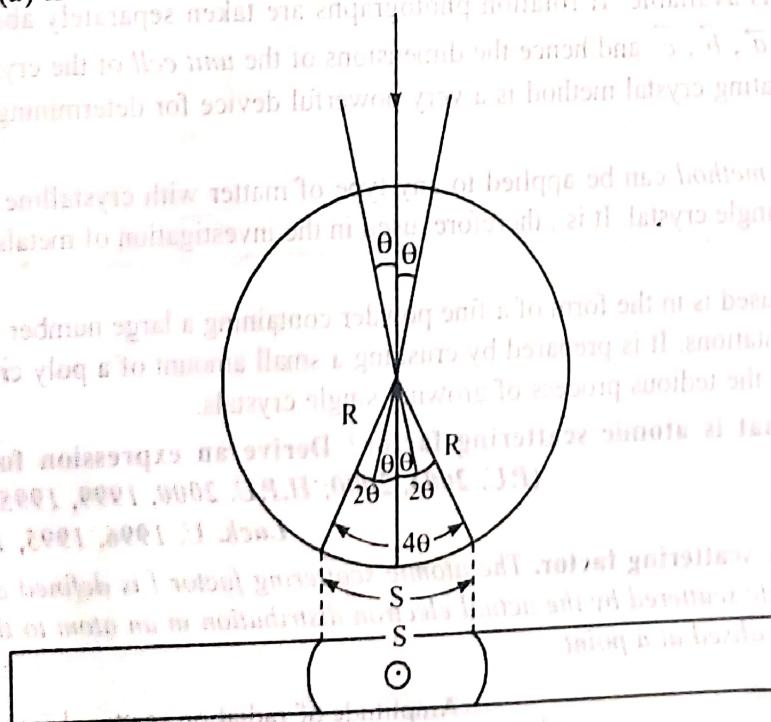


Fig. 2.7(a)

From the figure, we have  $4\theta = \frac{S}{R}$  radian  $= \frac{180}{\pi R} S$  degrees.



Now 
$$\frac{180}{\pi} = 57.3$$

$$4\theta \text{ (degrees)} = 57.3 \frac{S}{R}$$

The calculation can be made simple by taking  $R = 57.3$  mm or a multiple of that because the glancing angle can be directly calculated. If we take  $R = 57.3$  mm, then

$$\theta \text{ (degrees)} = \frac{S}{4} \text{ mm}$$

Thus, one fourth of the distance between the corresponding arcs of a particular pair in mm is a measure of angle  $\theta$  in degrees.

*This is why the diameter of the powder camera is 57.3 mm or a multiple of that.*

(c) **Usefulness of Laue, rotating crystal and powder methods.** The *Laue method* is suitable for the rapid determination of crystal orientation and symmetry. For example, if the crystal has four fold axial symmetry and is so oriented that its axis is parallel to the X-ray beam, the resulting Laue pattern will also show four fold symmetry. The symmetry of the pattern helps to determine the shape of the unit cell.

An imperfect or strained crystal has atomic planes which are not exactly plane but are slightly curved. Therefore, instead of sharp diffraction spots we get streaks in Laue's pattern. The formation of streaks on Laue's photographs is known as *asterism*.

This method is, therefore, used for studying the extent of crystalline imperfection under mechanical and thermal treatment.

This method is not suitable for determining crystal structure. It is because out of the continuous range of wavelengths, several wavelengths are reflected in different orders from a single plane and hence different order reflections may overlap on a single spot.

The *rotating crystal method* is the best suited method for structure determination when single crystal specimen is available. If rotation photographs are taken separately about three axes the translation vector  $\vec{a}$ ,  $\vec{b}$ ,  $\vec{c}$  and hence the dimensions of the *unit cell* of the crystal is determined. Therefore, the rotating crystal method is a very powerful device for determining the size of a unit cell.

The powder method can be applied to any type of matter with crystalline arrangement as it does not require single crystal. It is, therefore, used in the investigation of metals and alloys and applied work.

The sample used is in the form of a fine powder containing a large number of tiny crystallites with random orientations. It is prepared by crushing a small amount of a polycrystalline material. Thus it eliminates the tedious process of growing single crystals.

**Q. 2.12** What is atomic scattering factor? Derive an expression for it. Explain its significance.  
(P.U. 2004, 2000; H.P.U. 2000, 1999, 1995; G.N.D.U. 2000; Luck. U. 1996, 1995, 1994; K.U. 1991)

**Ans. Atomic scattering factor.** The atomic scattering factor  $f$  is defined as the ratio of the radiation amplitude scattered by the actual electron distribution in an atom to that scattered by a single electron localised at a point.

or

$$f = \frac{\text{Amplitude of radiation scattered from an atom}}{\text{Amplitude of radiation scattered from an electron}}$$

The value of  $f$  depends upon the number and distribution of electrons in an atom and wavelength and angle of scattering of the radiation wave.

To calculate the atomic scattering (or form) factor arrange the co-ordinate system in such a way that the incident and reflected wave normals make equal angles with the normal  $\vec{S}$  to the reflecting plane at  $A$  the centre of the atom as shown.

Let the incident wave normal and the reflected (or scattered) wave normal make an angle  $\theta$  with the reflecting or scattering plane corresponding to Bragg reflection.

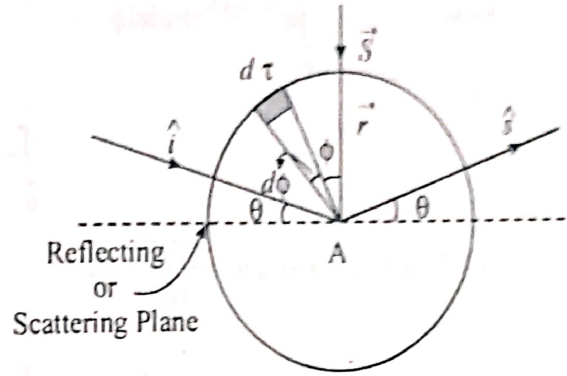


Fig. 2.8

Now consider an element of charge  $\rho(r) d\tau$  in a small volume  $d\tau$  at the position  $(r, \phi)$ .  $\rho(r)$  defines the contribution of the atom to the electron concentration at  $\vec{r}$ .  $\rho(r) d\tau$  represents the probability of finding the electron in the element of volume  $d\tau$  at  $\vec{r}$ . The phase difference between the radiation scattered by the element of charge  $\rho(r) d\tau$  at  $(r, \phi)$  and the radiation that would be scattered by the same amount of charge located at the centre of the atom is given by

$$\phi_r = \frac{2\pi}{\lambda} (\vec{r} \cdot \vec{S}) \quad \dots(i)$$

where

$$|\vec{S}| = 2 \sin \theta$$

Let the amplitude of the wave scattered from the point electron at  $A$  in the direction of unit vector  $\hat{s}$  be represented by  $Ae^{i(kx - \omega t)}$  where  $x$  is the distance co-ordinate along  $\hat{s}$ ,  $k$  is the magnitude of the wave vector i.e.,  $|\vec{k}| = \frac{2\pi}{\lambda}$  and  $\omega$  is the angular frequency of the wave.

The amplitude of the scattered wave from the volume element  $d\tau$  in the same direction will be proportional to the amount of charge  $\rho(r) d\tau$  in the volume element  $d\tau$  and have a phase difference  $\phi_r$  stated in (i). It is given by

$$Ae^{i[(kx - \omega t) + \phi_r]} \rho(r) d\tau$$

The ratio of the amplitude of the radiation scattered by the element of charge  $\rho(r) d\tau$  at  $\vec{r}$  to that scattered by a point electron at the centre of the atom (or origin)

$$\begin{aligned} df &= \frac{Ae^{i[(kx - \omega t) + \phi_r]} \rho(r) d\tau}{Ae^{i(kx - \omega t)}} \\ &= e^{i\phi_r} \rho(r) d\tau \\ &= e^{i\left(\frac{2\pi}{\lambda}\right)(\vec{r} \cdot \vec{S})} \rho(r) d\tau \end{aligned}$$

Now

$$\vec{r} \cdot \vec{S} = rS \cos \phi = 2r \sin \theta \cos \phi$$

[See Q. 2.10]

$\therefore$

$$\begin{aligned} \left(\frac{2\pi}{\lambda}\right)(\vec{r} \cdot \vec{S}) &= \frac{4\pi}{\lambda} r \sin \theta \cos \phi \\ &= \mu r \cos \phi \end{aligned}$$

(where  $\frac{4\pi}{\lambda} \sin \theta = \mu$ )

Also

$$d\tau = 2\pi r^2 \sin \phi \, d\phi \, dr$$

as it is the volume of an annular ring of radius  $r \sin \phi$ , width  $r d\phi$  and thickness  $dr$

$$f = \int df = \int_0^\infty \int_0^\pi \rho(r) e^{i\mu r \cos \phi} 2\pi r^2 \sin \phi \, d\phi \, dr$$



Now 
$$\int_0^\pi e^{i\mu r \cos \phi} \sin \phi d\phi = \frac{2 \sin \mu r}{\mu r}$$

$$f = \int_0^\infty 4\pi r^2 \rho(r) \frac{\sin \mu r}{\mu r} dr$$

As  $\theta \rightarrow 0$   $\mu \rightarrow 0$  and  $\frac{\sin \mu r}{\mu r} \rightarrow 1$

$$\text{Lt. } \mu \rightarrow 0 \quad f = \int_0^\infty 4\pi r^2 \rho(r) dr$$

= Total number of electrons in the atom =  $Z$

because  $4\pi r^2 \rho(r) dr$  gives the probability that an electron lies between radii  $r$  and  $r + dr$ .

**Significance.** The atomic scattering factor  $f$  is equal to the total number of electrons  $Z$  in the atom for  $\theta = 0$ . For  $\theta > 0$  the atomic scattering factor is  $< Z$ . A knowledge of  $f$  gives the charge distribution in the atom.

In other words, the integrand  $\int_0^\infty 4\pi r^2 \rho(r) dr$  represents the charge inside a spherical shell of radius  $r$  and thickness  $dr$  and hence the integral gives the total electronic charge  $Z$  inside the atom (sphere).

**Q. 2.13 (a)** Define geometrical structure factor. How is it related to atomic scattering factor? Derive an expression for the scattering amplitude in terms of geometrical structure factor.

(b) Calculate the geometrical structure factor for simple cubic (sc), body centred cubic (bcc) and face centred cubic (fcc) lattices.

(c) Explain the fact that (100) (300) reflection lines vanish for metallic sodium but not for Cs Cl, both have (bcc) structure. Also explain that in metallic sodium (200) reflection is present.

(H.P.U. 2003, 2002, 2001, 1997, 1994; G.N.D.U. 1999; 1996; P.U. 2001, 1994; Pbi. U. 2001; Luck. U. 2001)

**Ans. (a)** Geometrical structure factor. It is defined as the ratio of the amplitude of the wave scattered by an entire unit cell to the amplitude of the wave scattered by a single point electron for the same wavelength at the origin.

**Scattering amplitude in terms of geometrical structure factor.** The structure of all crystals is described in terms of a lattice with a group of atoms attached to each lattice point. The group is called the basis. It is repeated in space to form the crystal structure; every basis being identical in composition, arrangement and orientation. The number of atoms in a basis may be one as in many metals and inert gases but can be as large as one thousand. The position of the centre of the atom of the basis is written as

$$\vec{r}_j = x_j \vec{a} + y_j \vec{b} + z_j \vec{c}$$

relative to the lattice point. It is so arranged that  $x_j$ ,  $y_j$  and  $z_j$  lie between 0 and 1 i.e.,  $0 \leq x_j, y_j, z_j \leq 1$ .

The structure amplitude is denoted as  $|\vec{F}(hkl)|$  for a given  $(hkl)$  reflection and is given by

$$|\vec{F}(hkl)| = \sum f_j e^{i\phi_j} = \sum f_j e^{i\left(\frac{2\pi}{\lambda}\right)(\vec{r}_j \cdot \vec{s})}$$

Crystal Diffraction and Reciprocal Lattice

where  $f_j$  is the atomic scattering factor

scattered at the origin and that scattered at the origin to the  $j$ th atom,  $\vec{S}$  a vector normal to all the atoms in the unit cell.

Now

where  $x_j$ ,  $y_j$  and  $z_j$  are the fractional coordinates of the  $j$ th atom.

But  $\vec{a} \cdot \vec{S}$

Hence  $|\vec{F}(hkl)|$

When all the atoms are identical,  $F(hkl) = f \sum e^{i\phi_j}$

where

and is known as geometrical structure factor of atoms within the unit cell.

Thus we can define the geometrical structure factor  $F(hkl)$  to that of atom  $f$ .

Relation: Geometrical structure factor

Since the intensity of radiation is proportional to the square of the amplitude of the diffracted beam may be written as  $I = F^2$  where  $F = F(hkl)$

$I = F^2$

(b) 1. Geometrical structure factor. In a simple cubic crystal there is only one atom per unit cell.

and

Therefore, all the lines of a simple cubic crystal have a structure factor sufficiently large to be observed.

2. Body centred cubic (bcc) structure. In a bcc unit cell, one contributed by the corner atom and one by the body centred atom.



where  $f_j$  is the atomic scattering factor,  $\phi_j = \frac{2\pi}{\lambda} (\vec{r}_j \cdot \vec{S})$  = phase difference between the wave scattered at the origin and that scattered from the  $j$ th atom of the unit cell,  $\vec{r}_j$  the vector from the origin to the  $j$ th atom,  $\vec{S}$  a vector normal to the reflecting plane and  $\sum$  gives the summation over all the atoms in the unit cell.

$$\text{Now } \vec{r}_j = x_j \vec{a} + y_j \vec{b} + z_j \vec{c}$$

where  $x_j, y_j$  and  $z_j$  are the fractional co-ordinates of the  $j$ th atom i.e., their values lie between 0 and 1.

$$\begin{aligned} \therefore \vec{r}_j \cdot \vec{S} &= (x_j \vec{a} + y_j \vec{b} + z_j \vec{c}) \cdot \vec{S} \\ &= x_j (\vec{a} \cdot \vec{S}) + y_j (\vec{b} \cdot \vec{S}) + z_j (\vec{c} \cdot \vec{S}) \end{aligned}$$

$$\text{But } \vec{a} \cdot \vec{S} = h\lambda, \vec{b} \cdot \vec{S} = k\lambda \text{ and } \vec{c} \cdot \vec{S} = l\lambda$$

$$\text{Hence } |\vec{F}(hkl)| = \sum_j f_j e^{i2\pi(hx_j + ky_j + lz_j)}$$

When all the atoms are identical, all the  $f_j$ 's have the same value say  $f$  and we have

$$F(hkl) = f \&$$

$$\text{where } \& = \sum_j e^{i2\pi(hx_j + ky_j + lz_j)} = \frac{F(hkl)}{f}$$

and is known as *geometrical structure factor* because it depends upon the geometrical arrangement of atoms within the unit cell.

Thus we can define the geometrical structure factor  $\&$  as the ratio of the total scattering amplitude  $F(hkl)$  to that of atomic scattering factor  $f$ .

$$\text{Relation: Geometrical structure factor } \& = \frac{\text{Total scattering amplitude } F(hkl)}{\text{Atomic scattering factor } f}$$

Since the intensity of radiation is proportional to the square of its amplitude, the intensity of the diffracted beam may be written as  $I = |F|^2 = F F^*$

where  $F = F(hkl)$  and  $F^*$  its complex conjugate

$$\therefore I = \left[ \sum_j f_j \cos 2\pi(hx_j + ky_j + lz_j) \right]^2 + \left[ \sum_j f_j \sin 2\pi(hx_j + ky_j + lz_j) \right]^2$$

**(b) 1. Geometrical structure factor for simple cubic crystal (sc lattice).** For simple cubic crystal there is only one atom per unit cell at the origin, so that

$$x_j = y_j = z_j = 0$$

$$\text{and } F(hkl) = f$$

Therefore, all the lines predicted by Bragg's law will occur provided the atomic scattering factor is sufficiently large to make the intensity peaks visible.

**2. Body centred cubic lattice (bcc).** The basis of the bcc structure has two identical atoms per unit cell, one contributed by the corner atoms of the cell and the other at the centre of the cell. For the corner atom let

$$x_1 = y_1 = z_1 = 0$$

$$(j = 1)$$



Then for the body centre atom  $x_2 = y_2 = z_2 = \frac{1}{2}$

The diffraction amplitude for  $(hkl)$  direction

$$F(hkl) = f \sum_j e^{i2\pi(hx_j + ky_j + lz_j)} \\ = f(1 + e^{i\pi(h+k+l)})$$

substituting  $x_1 = y_1 = z_1 = 0$  for the first term and  $x_2 = y_2 = z_2 = \frac{1}{2}$  for the second term; where  $f$  is atomic form factor.

For any  $(hkl)$  reflection for which  $(h + k + l)$  is an odd integer  $e^{i\pi(h+k+l)} = -1$ .

$$\therefore F(hkl) = f(1 - 1) = 0$$

For a reflection for which  $(h + k + l)$  is an even integer

$$e^{i\pi(h+k+l)} = +1$$

$$\therefore F(hkl) = f(1 + 1) = 2f$$

**3. Face centred cubic lattice (fcc).** The basis for the *fcc* structure has four identical atoms per unit cell, one contributed by the corner atoms and three contributed by the face centre atoms. The four atoms have co-ordinates

$$(000) \left(0 \frac{1}{2} \frac{1}{2}\right) \left(\frac{1}{2} 0 \frac{1}{2}\right) \left(\frac{1}{2} \frac{1}{2} 0\right)$$

Thus the diffraction amplitude for the  $(hkl)$  reflection is given by

$$F(hkl) = f[1 + e^{i\pi(h+k)} + e^{i\pi(k+l)} + e^{i\pi(l+h)}]$$

If all the indices  $h, k, l$  are odd, then the amplitude

$$F(hkl) = f(1 + 1 + 1 + 1) = 4f$$

and intensity is proportional to  $(4f)^2 = 16f^2$ .

If only one of the indices say  $h$  is odd and the other two  $k$  and  $l$  are even, then  $e^{i\pi(h+k)} = -1$  and  $e^{i\pi(k+l)} = +1$ .

Hence  $F(hkl) = f(1 - 1 - 1 + 1) = 0$  and intensity is also zero. Similarly if one of the indices is even and the other two are odd  $F(hkl)$  is zero and intensity is also zero. Thus in an *fcc* lattice a reflection can occur for which the integers are partly even and partly odd.

**(c) Case of metallic sodium.** Metallic sodium has a *bcc* structure. The diffraction spectrum of metallic sodium does not contain lines such as (100), (300), (111) or (221) because  $(h + k + l)$  is an odd integer but lines such as (200), (110) and (222) will be present because  $(h + k + l)$  is an even integer, the indices  $(hkl)$  being referred to a cubic cell.

Let us explain why (100) reflection vanishes for a body centred cubic lattice whereas it is present for a simple cubic structure of the same cube edge dimensions. The (100) reflection for

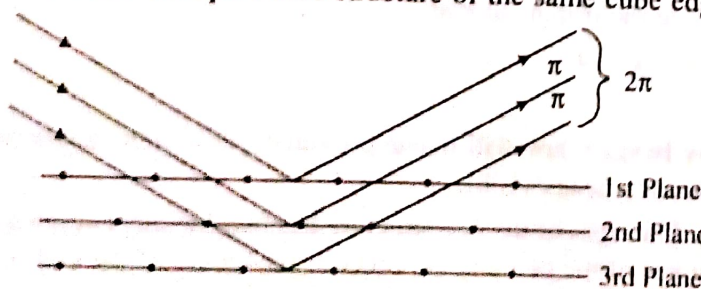


Fig. 2.9

simple cubic structure takes place when the beams reflected from the top and the bottom edges of the cube forming the unit cell differ in phase by  $2\pi$ .

For a *bcc* structure having the same cube edge dimensions, there is an intervening plane of atoms, labelled as the second plane in Fig. 2.9 situated midway between them, having a

scattering power equal to that of other planes. This *middle* plane gives a reflection out of phase by  $\pi$ . Thus the diffracted beams from the top planes and the body centre planes interfere *destructively* in pairs and give no net diffracted beam for (100) reflection.

However, in case the scattering power of the body centre plane is not equal to that of the top and bottom planes the intensity of (100) reflection and other similar reflections for which  $(h + k + l)$  is odd will not be zero. In such a case these reflections will have comparatively low intensity proportional to the square of the difference of the amplitudes of the scattered waves of the planes under consideration.

For example, in the case of Cs Cl, where the planes of Cs and Cl alternate, the cancellation does not occur because the scattering power of Cs is much greater than the scattering power of Cl because Cs has 54 electrons and Cl has only 18 electrons.

**Q. 2.14** What is reciprocal lattice? Why it is so named? Derive the expression for the primitive translation vectors of the reciprocal lattice. How is reciprocal lattice constructed? List its important properties.

(G.N.D.U. 2004, 2002; P.U. 2001, 2000, 1999, 1997, 1995, 1994; H.P.U. 2000, 1997, 1996; Pbi. U. 1999, 1997; Meerut U. 2001; Luck. U. 2001; M.D.U. 1999; A.U. 1995 1994)

**Ans. Reciprocal lattice.** Every crystal has two lattices associated with it, the crystal lattice (or direct space lattice) and the reciprocal lattice.

The concept of reciprocal lattice was devised for the purpose of tabulating two important properties of crystal planes; their *slope* and their *interplanar spacing*.

Each set of parallel planes in a direct lattice can be represented by a *normal* to these planes having length equal to the reciprocal of the interplanar spacing. The normals are drawn with reference to any arbitrary origin and points are marked at their ends. *These points form a regular arrangement which is called reciprocal lattice*. Thus each point in a reciprocal lattice is a representative point of a particular parallel set of planes. It is easier to deal with such points than to deal with set of planes. This is why we use reciprocal lattice.

Thus reciprocal lattice vector is a vector whose magnitude is equal to the reciprocal of the inter planar spacing i.e.,  $\frac{1}{d_{hkl}}$  and direction is parallel to the normal to (hkl) plane.

**Why reciprocal lattice is so named?** The reciprocal lattice is so named because the length assigned to each normal representing the reciprocal lattice is proportional to the reciprocal of the interplanar spacing of that plane in ordinary space.

**Primitive translation vectors of reciprocal lattice.** Let  $\vec{a}$ ,  $\vec{b}$ ,  $\vec{c}$  be the primitive translation vectors of a direct space lattice for a crystal forming a primitive unit cell. The volume of this unit cell is given by

$$V = \vec{a} \cdot (\vec{b} \times \vec{c}) = \vec{b} \cdot (\vec{c} \times \vec{a}) = \vec{c} \cdot (\vec{a} \times \vec{b})$$

The vectors given by

$$\vec{A} = 2\pi \frac{\vec{b} \times \vec{c}}{\vec{a} \cdot (\vec{b} \times \vec{c})}$$

$$\vec{B} = 2\pi \frac{\vec{c} \times \vec{a}}{\vec{b} \cdot (\vec{c} \times \vec{a})}$$

and

$$\vec{C} = 2\pi \frac{\vec{a} \times \vec{b}}{\vec{c} \cdot (\vec{a} \times \vec{b})}$$

are known as *reciprocal lattice vectors* or *primitive translation vectors of reciprocal lattice*.